^{11}B NMR spectra were recorded while the variable-temperature controller was used to maintain the desired probe temperature. Spectra were obtained at the following temperatures (observed Lorentzian line width): +60 °C (21 Hz), +40 °C (25 Hz), ambient (30 Hz), −40 °C (80 Hz). Neither the resonance frequency of **1** (δ −26.6) nor the symmetry of the peak was observed to change with either heating or cooling of the sample.

(^{1}H, ^{13}C) HETCOR Spectroscopy of 1 in THF-d_8. A sample of **1** in THF-d_8 was placed in a 5-mm NMR sample tube. The sample was freeze–pump–thaw degassed and the tube sealed. A HETCOR experiment was performed. From the ^{1}H, ^{13}C, and 2-D NMR data, the assignments shown in Table I were made. The carbon resonances at δ 37.2 and 135.5 are broadened due to coupling to boron.

Variable-Temperature ^{1}H NMR Spectroscopy of 1. A solution of **1** in THF-d_8 (0.5 mL) was placed in a 5-mm NMR sample tube. The sample was freeze–pump–thaw degassed, and the tube was sealed. The temperature of the NMR probe was regulated by use of the variable-temperature controller, and ^{1}H NMR spectra were obtained at the following temperatures: 20.0, −1.0, −5.0, −10.0, −15.0, −20.0, −25.0, −30.0, −40, −50, −60, −70, −80, −90, −100 °C. When the solution was cooled to −5.0 °C, the resonances assigned to the phenyl groups attached to boron (7.10, 6.81, 6.68) began to broaden. Further cooling resulted in additional broadening until at −80 °C these broadened peaks once again sharpened into multiplets. At −80 °C, the ^{1}H NMR spectrum showed the presence of two unique phenyl groups attached to boron. All other resonances were unaffected by cooling, except for minor changes in chemical shift. No further change in the appearance of the spectrum was observed upon cooling below −80 °C. Table II summarizes the observed changes.

The triplet at δ 6.81 was chosen for the calculation of kinetic and thermodynamic parameters since it appeared in a relatively clean region of the spectrum and split symmetrically upon cooling (6.88, 6.72 at −80.0 °C). The coalescence temperature of this resonance was determined to be ca. −20 °C.

Cyclic Voltammetry of 1 in Acetonitrile. A solution of **1** in acetonitrile containing tetrabutylammonium perchlorate as supporting electrolyte was oxidized with use of a glassy carbon electrode and a platinum counter electrode. An irreversible oxidation peak was observed at E_p −1.06 ± 0.02 V vs Ag/AgNO$_3$. Ferrocene was subjected to the cyclic voltammetry conditions as a standard. The reversible oxidation of this species occurred at 0.072 V under these conditions.

Triplet Sensitization of (p-Biphenylyl)triphenylborate with N-Phenylcarbazole Followed by ^{11}B NMR Spectroscpy. A 3-mL volume of an acetonitrile solution of N-phenylcarbazole (1.29×10^{-2} M) and **4** (1.11×10^{-2} M) was placed in a 10-mm NMR sample tube. The tube was fitted with a septum, and the sample was purged with nitrogen for 5 min. The sample was irradiated at 350 nm under nitrogen and monitored periodically by ^{11}B NMR spectroscopy. After 10 min of irradiation, the ^{11}B NMR spectrum revealed an ~10% conversion of starting borate and the presence of a single product at δ −26.6 (i.e., borate **1**). After 30 min of irradiation, ~20% of the starting borate had reacted.

A solution of (p-biphenylyl)triphenylborate (1.11×10^{-2} M) treated in the same manner showed no reaction after 10 min of irradiation.

Acknowledgment. This work was supported by a grant from the National Science Foundation for which we are grateful. We thank David Hartsough and Professor Scott Kahn of this Department for their assistance with the molecular orbital calculations and Dr. Scott Wilson of the University of Illinois X-ray laboratory for his assistance with the structure determination.

Photochemistry of Alkynyl-, Alkenyl-, and Cyclopropyl-Substituted Borate Salts: The Di-π- and Cyclopropyl-π-borate Rearrangements

Michael A. Kropp, Michelle Baillargeon, Kyung Mi Park, Kaumudi Bhamidapaty, and Gary B. Schuster*

Contribution from the Department of Chemistry, Rodger Adams Laboratory, University of Illinois, Urbana, Illinois 61801-3731. *Received August 13, 1990*

Abstract: The photochemistry of potassium triphenyl(phenylethynyl)borate (**1**), tetramethylammonium triphenyl(*trans*-β-styryl)borate (**2**), and cesium phenyl(2-phenylcyclopropyl)dimethylborate (**3**) was studied. When irradiated with UV light, these compounds undergo rearrangements to generate potassium 1,1,2,3-tetraphenylboratirene (**4**), tetramethylammonium *trans*-1,1,2,3-tetraphenylboratirane (**5**), and (unisolated) cesium 1,1-dimethyl-2,4-diphenylboratetane (**6**), respectively. The mechanism of these reactions appears to be similar to the di-π-methane and cyclopropyl-π-methane routes for the analogous hydrocarbons. The effect of borate structure on the efficiency of these reactions was analyzed. Additionally, the chemical and physical properties of the small-ring borates were probed.

The first systematic investigation of the photochemistry of organic borates was carried out by Williams and co-workers.[1] Subsequent studies confirmed their suggestion that a formal [1,2] sigmatropic rearrangement of a phenyl group leads to intermediates containing a bridging borate group. In particular, we showed that irradiation of tetramethylammonium tetraphenylborate gives 2,7,7-triphenyl-7-boratabicyclo[4.1.0]hepta-2,4-diene.[2] Similarly, we isolated and characterized by X-ray crystallography the bridged borate formed by irradiation of tetramethylammonium (p-biphenylyl)triphenylborate.[3] In 1975, Eisch and co-workers suggested that a related rearrangement occurs when lithium triphenyl(phenylethynyl)borate is irradiated with UV light.[4] In more recent work, this group reported the successful isolation and characterization of triarylborirenes formed by a [1,2] aryl group rearrangement when diaryl(arylethynyl)boranes are irradiated in donor-containing solvents.[5]

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[1] (a) Williams, J. L. R.; Grisdale, P. J.; Doty, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 4538. (b) Williams, J. L. R.; Doty, J. C.; Grisdale, P. J.; Searle, R.; Regan, T. H.; Happ, G. P.; Maier, D. P. *J. Am. Chem. Soc.* **1967**, *89*, 5153. (c) Williams, J. L. R.; Doty, J. C.; Grisdale, P. J.; Regan, T. H.; Happ, G. P.; Maier, D. P. *J. Am. Chem. Soc.* **1968**, *90*, 53. (d) Williams, J. L. R.; Grisdale, P. J.; Doty, J. C.; Glogowski, M. E.; Babb, B. E.; Maier, D. P. *J. Organomet. Chem.* **1968**, *14*, 53. (e) Grisdale, P. J.; Babb, B. E.; Doty, J. C.; Regan, T. H.; Maier, D. P.; Williams, J. L. R. *J. Organomet. Chem.* **1968**, *4*, 63. (f) Grisdale, P. J.; Williams, J. L. R.; Glogowski, M. E.; Babb, B. E. *J. Org. Chem.* **1971**, *36*, 544.

[2] Wilkey, J. D.; Schuster, G. B. *J. Org. Chem.* **1987**, *52*, 2117. See previous paper in this issue.

[3] Wilkey, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 7569.

[4] Eisch, J. J.; Tamao, K.; Wilcsek, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 895.

[5] (a) Eisch, J. J.; Shafii, B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 2526. (b) Eisch, J. J.; Shafii, B.; Odom, J. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 1847.

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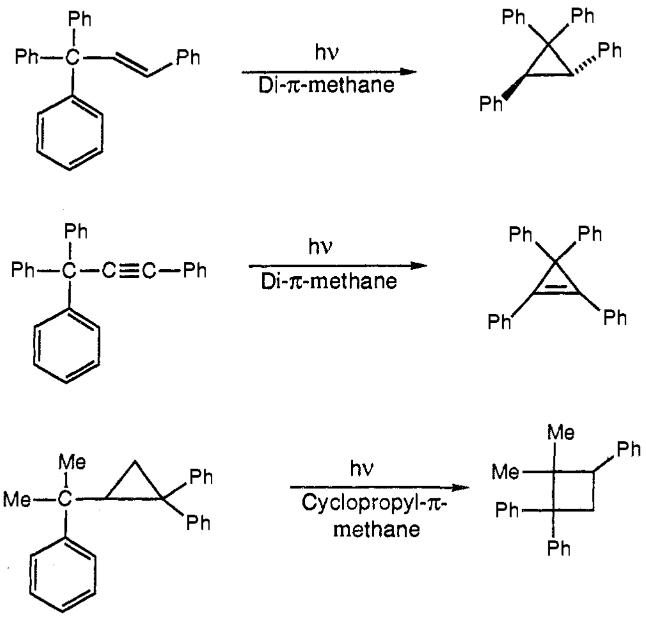
Scheme I



The di-π-methane rearrangement of hydrocarbons (also formally a [1,2] sigmatropic rearrangement) has been extensively studied. In particular, Griffin and co-workers[6] showed that photolysis of *trans*-1,3,3,3-tetraphenylpropene gives *trans*-1,1,2,3-tetraphenylcyclopropane and that 1,3,3,3-tetraphenylpropyne gives tetraphenylcyclopropene by a process that has come to be generally recognized as the di-π-methane rearrangement (Scheme I). Similarly, Zimmerman and co-workers[7] report that photolysis of 1,1-diphenyl-2-(α,α-dimethylbenzyl)cyclopropane undergoes a [1,2] phenyl group shift identified as a cyclopropyl-π-methane rearrangement to give 1,1-dimethyl-2,2,4-triphenylcyclobutane (albeit, in low yield) (Scheme I). The mechanism of di-π-methane-like rearrangements has been studied extensively.[8]

On the basis of these findings, we considered that the photochemistry of appropriate borate salts might generally parallel the di-π-methane rearrangements of their hydrocarbon analogues. Herein, we report the results of photolysis of potassium triphenyl(phenylethynyl)borate (**1**),[9] tetramethylammonium triphenyl(*trans*-β-styryl)borate (**2**),[10] and cesium phenyl(2-phenylcyclopropyl)dimethylborate (**3**). The irradiation of these borates with UV light gives potassium 1,1,2,3-tetraphenylboratirene (**4**), tetramethylammonium *trans*-1,1,2,3-tetraphenylboratirane (**5**), and (unisolated) cesium 1,1-dimethyl-2,4-diphenylboratetane (**6**), respectively (Chart I). The chemical and physical properties of these small-ring borates are also described.

Results

(1) Irradiation of Triphenyl(phenylethynyl)borate (1). The UV-vis absorption spectrum of borate **1** in acetonitrile solution has a maximum at 259 nm (ϵ_{max} = 19000 M^{-1} cm^{-1}). The ^{11}B NMR spectrum of this salt shows a single resonance at δ −12 in acetonitrile solution. Direct irradiation of borate **1** at 254 nm in oxygen-free THF solution causes the initially colorless solution to become deeply orange. The ^{11}B NMR spectrum of the photolysis mixture shows new resonances at δ −16 and −36 in a ratio of 4:1. The same products are obtained when the irradiation is carried out in acetonitrile solution. However, no reaction is observed when triplet sensitization of borate **1** with xanthone is attempted.

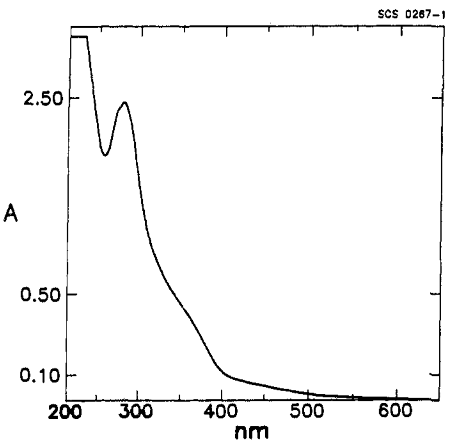
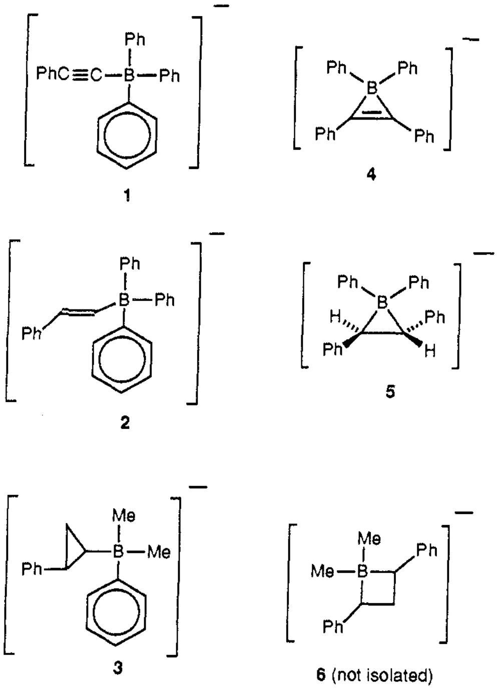
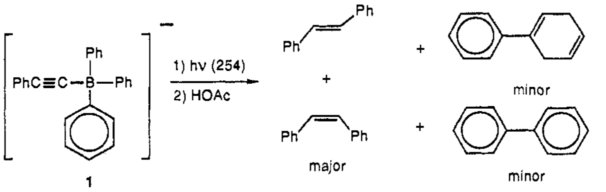


Figure 1. UV-vis absorption spectrum of potassium 1,1,2,3-tetraphenylboratirene (1.0 × 10^{-4} M) at room temperature in THF solution.

Chart I



Addition of acid to the product mixture obtained from direct irradiation of **1** gives *cis*- and *trans*-stilbene (45%) and biphenyl and dihydrobiphenyl (15%). The latter compound was isolated by preparative gas chromatography and identified by its ^1H NMR and UV spectra as 1-phenyl-1,4-cyclohexadiene as shown in eq 1. Formation of stilbenes indicates that a [1,2] migration of a phenyl group from boron to the acetylenic carbon atom has occurred. Similarly, biphenyl and dihydrobiphenyl formation signals bond formation between two of the phenyl groups bound to boron in the starting material.



(1)

The ^1H NMR spectrum of the photolysis mixture (in THF-d_8) shows aromatic hydrogen resonances for the major product and a set of nonaromatic region resonances characteristic of a bora-

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[6] (a) Griffin, G. D.; Marcantonio, A. F.; Kristinsson, H.; Petterson, R. C.; Irving, C. S. *Tetrahedron Lett.* **1965**, 2951. (b) Halton, B.; Kulig, M.; Battiste, M. A.; Perreten, J.; Gibson, D. M.; Griffin, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 2327.

[7] Zimmerman, H. E.; Carpenter, C. W. *J. Org. Chem.* **1988**, *53*, 3298.

[8] Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 131.

[9] Kropp, M. A.; Schuster, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 2316.

[10] Kropp, M.; Bhamidapity, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 6252.

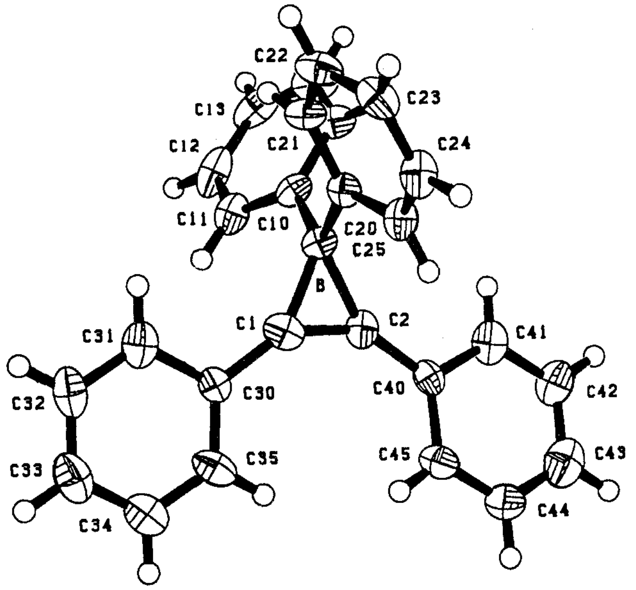
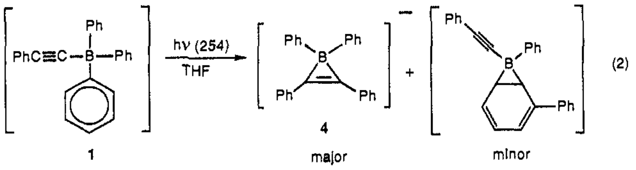


Figure 2. Structure of potassium 1,1,2,3-tetraphenylboratirene determined by X-ray crystallography (potassium cation not shown).

tanorcaradiene associated with the minor product.[2,3] A full description of this spectrum is given in the Experimental Section. The major product was isolated from the reaction mixture in 50% yield by its precipitation with hexane. Several recrystallizations from mixtures of THF and hexane give a pure, yellow, crystalline solid.

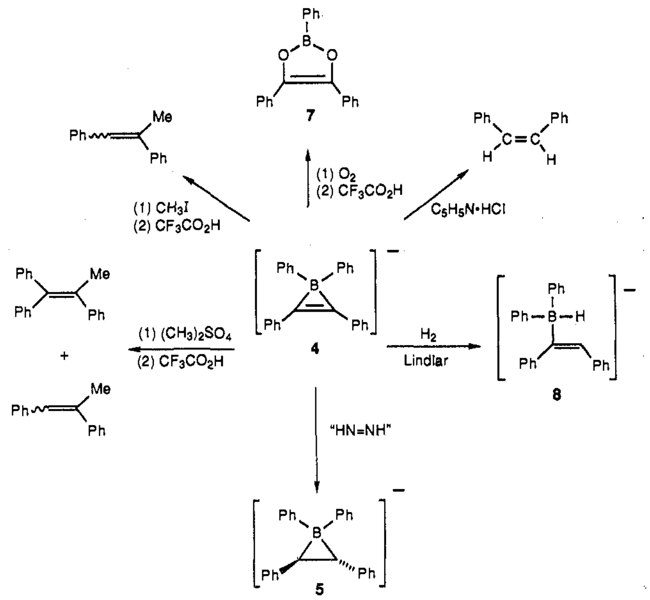
Elemental analysis of the isolated photoproduct proves it to be an isomer of borate **1**. Its ^{11}B NMR spectrum shows a single sharp peak at δ −16.1, which corresponds to the major product in the photolysis mixture. Its UV–vis absorption spectrum at room temperature in THF solution is shown in Figure 1. There is a strong absorption at 269 nm (ϵ_{max} = 21 500 M^{-1} cm^{-1}) and weaker bands with apparent maxima at 350 and 450 nm (ϵ_{max} = 4500 and 600 M^{-1} cm^{-1}, respectively). When oxygen or water is added to the sample, both of the weaker absorption bands disappear. The spectrum of the photoproduct was recorded in frozen 2-methyltetrahydrofuran solution at 77 K to probe the temperature dependence of the 350- and 450-nm bands. The intensities of these bands appear to increase at the low temperature due to contraction of the solution. This observation shows that the color of the photoproduct is not due to the presence of a strongly absorbing minor component in equilibrium with the principal component that is observable by NMR spectroscopy.[11]

The ^1H NMR spectrum of the major product from irradiation of borate **1** shows only absorptions characteristic of hydrogens bound to phenyl groups. As its tetraphenylarsonium salt, the spectrum of the borate shows six resonances. There are four multiplets, each corresponding to four hydrogens, and two multiplets, each integrating for two hydrogens. The ^{13}C NMR spectrum of this product shows resonances for only nine carbon atoms; two of these (δ 161.1 and 149.5) are strongly coupled to the boron atom. On the basis of these spectroscopic findings, the major photoproduct was deduced to be potassium tetraphenylboratirene (**4**), eq 2. This assignment was proven by X-ray crystallography.



(2) Structure and Reactivity of Tetraphenylboratirene (4). Figure 2 shows the structure of boratirene **2** determined by X-ray crystallography.[12] The borate-containing three-membered ring has a C–B–C bond angle of 50.6 (3)° and the two C–C–B bond angles are 65.4 (4)° and 64.0 (4)°. The ring carbon–carbon bond length is 1.357 (7) Å, and the carbon–boron bond lengths are 1.578 (8) and 1.597 (8) Å. The carbon–carbon bond length for the boratirene falls within the range normally observed for phenyl-substituted cyclopropenes.

Scheme II



With the structure of borate **4** clearly established, we undertook an investigation of its chemical and physical properties. These results are summarized in Scheme II.

cis-Stilbene is formed in essentially quantitative yield when pyridine hydrochloride is added to a THF solution of **4**. Borate **4** reacts rapidly with oxygen to give, after acidic workup, 2,4,5-triphenyl-1,3-dioxa-2-borole (**7**) as primary product and small amounts of *cis*- and *trans*-stilbene.

Hydrogenation of boratirene **4** with Lindlar's catalyst initiates reductive cleavage of the three-membered ring to give borohydride **8** as the primary product. Reaction of **4** with diimide, formed from in situ thermolysis of anthracene-9,10-diimine,[13] yields *trans*-1,1,2,3-tetraphenylboratirane (**5**). Since reductions with diimide occur with retention of configuration,[14] we presume that the first-formed product of this reaction is the *cis*-boratirane but that isomerization to the more stable trans isomer occurs under the reaction conditions.

The reactions of boratirene **4** with electrophiles parallel those observed by Negishi for tri-*n*-butyl-1-naphthylborate.[15] Two paths whose identity seems to depend on the nature of the electrophile are observed. When dimethyl sulfate is added to boratirene **4**, *cis*- and *trans*-α-methylstilbenes and 1,1,2-triphenylpropane are found after acidic workup. When the electrophile is methyl iodide, the products are *cis*- and *trans*-stilbene and *cis*- and *trans*-α-methylstilbene, but none of the phenyl group shifted triphenylpropane is observed.

The reactions of boratirene **4** with oxygen and methyl iodide may be initiated by single-electron transfer. We attempted to measure the oxidation potential of **4** by cyclic voltammetry. An acetonitrile solution containing tetrabutylammonium perchlorate as supporting electrolyte gives an irreversible oxidation wave at −0.6 V vs Ag/$AgNO_3$. Thus, it is clear that boratirene **4** is a powerful reducing agent.

(3) Irradiation of Cesium Dimethylphenyl(phenylethynyl)borate. Substitutent Effects in the Di-π-borate Rearrangement. Zim-

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[11] Eisch, J. J. *Chem. Eng. News* **1989**, *67*, 3.

[12] A detailed description of the X-ray data is available as supplementary material to ref 9.

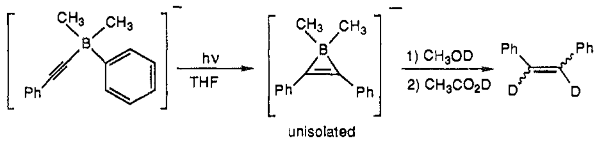
[13] Corey, E. J.; Mock, W. L. *J. Am. Chem. Soc.* **1962**, *84*, 685.

[14] Corey, E. J.; Pasto, D. J.; Mock, W. L. *J. Am. Chem. Soc.* **1961**, *83*, 2957.

[15] Negishi, E.; Merrill, R. E. *Chem. Commun.* **1974**, 860.

merman and co-workers showed that the di-π-methane rearrangement of hydrocarbons is somewhat sensitive to the nature of the substituents on the methane carbon atom. Systems lacking substituents at this position do not rearrange by the di-π-methane path when two vinyl groups compose the π systems.[16] However, Hixson showed that methane substituents are not required when one π moiety is a phenyl group.[17] Zimmerman and co-workers further studied the influence of methane-substituent structure and found that two methyl groups were only little worse than two phenyl groups in promoting the di-π-methane rearrangement.[18] We explored the consequence of the related change of two phenyl groups on borate **1** to methyl groups.

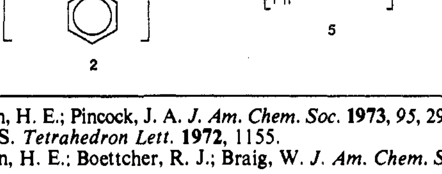
An oxygen-free THF solution of cesium phenyl(phenylethynyl)dimethylborate (eq 3; the cesium salt was chosen because it is both solid and soluble in THF) was irradiated at 254 nm in a Rayonet photoreactor. Analysis of the reaction solution by means of ^{11}B NMR spectroscopy showed the slow consumption of the starting borate (δ -20.4) but no new resonances that could be attributed to a boratirene. However, when the irradiation of phenyl(phenylethynyl)dimethylborate was performed in THF containing CH_3OD and then worked up by the addition of CH_3CO_2D, a 34% yield of *cis*- and *trans*-1,2-dideuteriostilbene was obtained. The appearance of the dideuteriostilbene signals the likely intermediate formation of *B*,*B*-dimethyl-2,3-diphenylboratirene as shown in eq 3.



(3)

(4) Irradiation of Triphenyl(*trans*-β-styryl)borate (2). The UV–vis absorption spectrum of borate **2** in acetonitrile solution has a maximum at 270 nm (ϵ_{max} = 23 000 M^{-1} cm^{-1}) characteristic of its styryl chromophore. The ^{11}B NMR spectrum of this salt shows a single resonance at δ -9.1 in acetonitrile solution. Direct irradiation of borate **2** at 254 nm in oxygen-free acetonitrile solution leads to the formation of a single product detected by an absorption at δ -9.4 in the ^{11}B NMR spectrum of the photolysis mixture. No reaction is observed when triplet sensitization of borate **2** with xanthone is attempted.

The product from irradiation of borate **2** was isolated as a white powder in 60% yield by concentration of the reaction mixture and then precipitated with ether. Recrystallization from a mixture of acetonitrile and ether gives the pure product shown to be isomeric with the starting material by elemental analysis. The UV spectrum of the product shows a single maximum at 280 nm (ϵ_{max} = 18 000 M^{-1} cm^{-1}). Its ^{1}H NMR spectrum shows a singlet at δ 2.39 corresponding to two hydrogen atoms in addition to a singlet for the tetramethylammonium group and absorptions in the aromatic region accounting for 20 hydrogen atoms. The ^{13}C NMR spectrum of the photoproduct shows only nine unique carbon resonances;[19] two (δ 38.3, 158) show one-bond coupling to boron. The spectroscopic results require a symmetry element in the photoproduct that makes two pairs of phenyl groups equivalent and leaves only one other unique, boron-coupled carbon atom. On the basis of these findings, we identified the photoproduct as *trans*-tetraphenylboratirane (**5**), eq 4. This assignment was proven by X-ray crystallography.



(4)

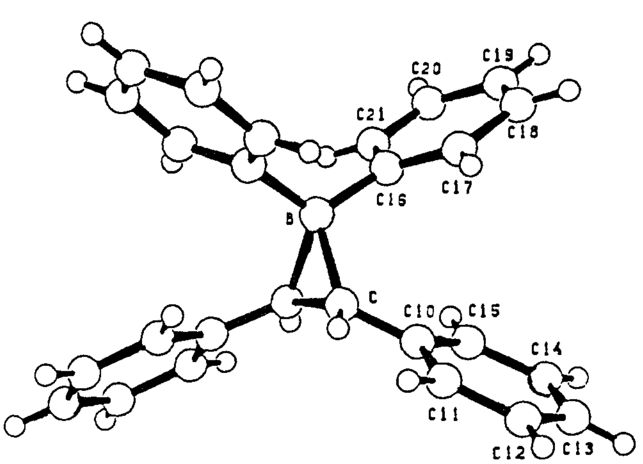
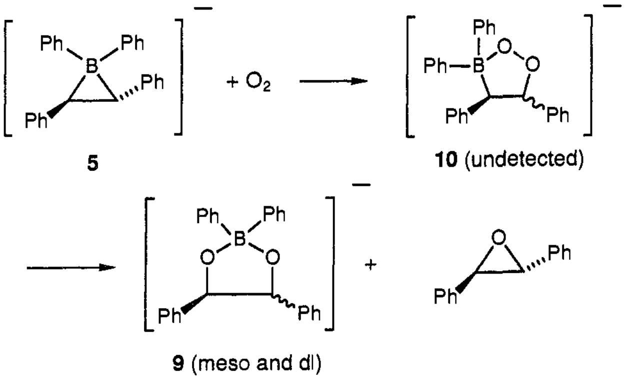


Figure 3. Structure of tetraphenylarsonium (not shown) *trans*-1,1,2,3-tetraphenylboratirane determined by X-ray crystallography.

Scheme III



(5) Structure and Reactivity of *trans*-Tetraphenylboratirane. The tetramethylammonium salt of tetraphenylboratirane did not give material useful for structure determination by X-ray crystallography. However, both the tetrabutylammonium and tetraphenylarsonium salts form suitable crystals. Figure 3 shows the structure of *trans*-tetraphenylboratirane determined by X-ray crystallography of the tetraphenylarsonium salt (there are no meaningful differences in the tetrabutylammonium salt).[20] The three-membered ring of the boratirane is an isosceles triangle with ∠CBC = 55 (1)° and ∠CCB = 62 (1)°. The ring carbon–boron bond distance is 1.61 (3) Å, and the carbon–carbon bond distance is 1.49 (3) Å.

When oxygen and water are excluded, boratirane **5** is stable indefinitely in the solid state or when dissolved in THF or acetonitrile. The boratirane is hydrolyzed by water (or methyl alcohol) to give bibenzyl. The addition of oxygen to a solution of the boratirane gives *trans*-stilbene oxide, tetraphenylboratolane (**9**), and a trace amount of *trans*-stilbene. These products presumably signal intermediary formation of peroxyborolane **10** as shown in Scheme III. The reaction of **5** with oxygen may occur by an electron-transfer pathway. Cyclic voltammetric measurements in acetonitrile solution show an irreversible oxidation wave for the boratirane at ca. -0.8 V vs $Ag/AgNO_3$.

(6) Irradiation of Cesium Phenyl(*trans*-styryl)dimethylborate. The effect of the nature of the borate-bound substituents on the di-π-borate rearrangement was probed by irradiation (300 nm) of an oxygen-free THF solution of cesium phenyl(*trans*-styryl)dimethylborate. Analysis of the photolysis solution by ^{11}B NMR spectroscopy shows the slow consumption of the starting material, but no new resonances consistent with the formation of *B*,*B*-dimethyl-2,3-diphenylboratirane were detected. When this reaction was performed in the presence of CH_3OD, 1,2-dideuterio-1,2-diphenylethane is found in 53% yield by gas chromatography. This

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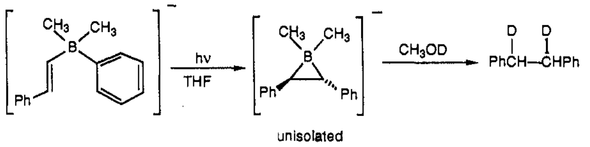
(16) Zimmerman, H. E.; Pincock, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 2957.
(17) Hixson, S. S. *Tetrahedron Lett.* **1972**, 1155.
(18) Zimmerman, H. E.; Boettcher, R. J.; Braig, W. *J. Am. Chem. Soc.* **1973**, *95*, 2155.
(19) There is a tenth resonance at δ 55.99 due to the tetramethylammonium counterion.

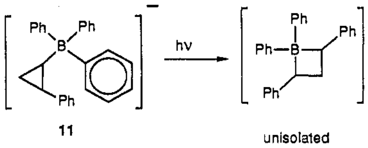
(20) A detailed description of the X-ray data is available as supplementary material to ref 10.

result signals the likely intermediate existence of the boratirane according to eq 5.



(5)

(7) Photochemistry of Cesium Phenyl(2-phenylcyclopropyl)dimethylborate (3). In an attempt to extend the range of known photochemical reactions of borates, we investigated the irradiation of the cis and trans isomers of tetramethylammonium (2-phenylcyclopropyl)triphenylborate (**11**). Analogy to the work of Zimmerman and co-workers[7] suggests a possible cyclopropyl-π-borate rearrangement with formation of a boratetane as shown in eq 6.

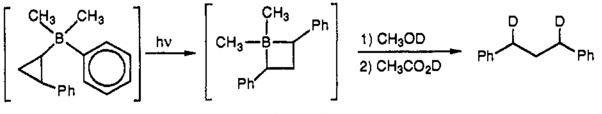


11

(6)

Examination of the ^{11}B NMR spectrum of the mixture formed from irradiation (254 or 300 nm) of cis borate **11** (similar results are obtained with the trans isomer) in acetonitrile shows formation of several products containing anionic tetravalent boron groups. When the photolysis is carried out in the presence of methyl alcohol, the products are biphenyl, dihydrobiphenyl, and 1,3-diphenylpropane formed in approximately equal yields. These findings indicate that the photolysis of **11** is proceeding along at least two competing paths. The dominant reaction is the coupling of a phenyl group to a phenyl group, which results in the formation of biphenyl and dihydrobiphenyl. The minor reaction is coupling of the phenyl and phenylcyclopropyl groups, which leads presumably to the boratetane and thence to 1,3-diphenylpropane. In an attempt to force the reaction to take the path leading to the desired boratetane, we prepared the tetrabutylammonium and cesium salts of phenyl(2-phenylcyclopropyl)dimethylborate 3. Since these compounds have only one phenyl group, the di-π-borate path is impossible and the cyclopropyl-π-borate path might be enhanced.

Several borate group containing products are detected by ^{11}B NMR spectroscopy when borate **3** is irradiated in oxygen-free THF solution. Gas chromatographic analysis of the photolysis solution after acidic workup shows formation of 1,3-diphenylpropane, *cis*- and *trans*-β-methylstyrene, and small amounts of toluene, styrene, and allylbenzene. When borate **3** is irradiated in a solution containing CH_3OD and the photolysis solution is worked up with CH_3CO_2D, the 1,3-diphenylpropane formed is 1,3-dideuteriated. The generation of dideuteriated diphenylpropane is consistent with formation of boratetane **6** as shown in eq 7. We suspect that secondary photolysis of **6** reduces its yield since the amount of 1,3-diphenylpropane formed is greater when methyl alcohol is present at the outset than is obtained when it is added after the irradiation is complete. Interestingly, amylbenzene, the product expected from trapping a benzyl anion equivalent, is formed when *n*-butyl bromide is present in the photolysis solution. Triplet sensitization of **3** with *N*-phenylcarbazole did not lead to reaction.



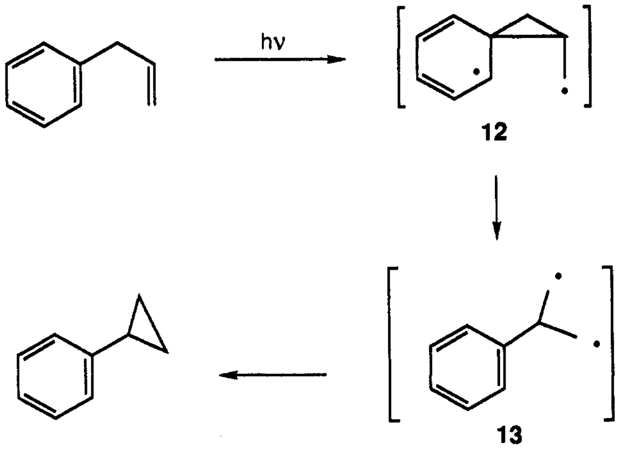
(7)

3 **6** (not isolated)

Discussion

(1) Mechanism of the Di-π-borate and the Cyclopropyl-π-borate Rearrangements. The mechanism of the di-π-methane rearrangement has been the subject of extensive and intensive study.[8] It is usually found that acyclic examples proceed through the singlet excited state of the hydrocarbon and that cyclic compounds react more often by a route through the triplet state. Moreover, careful investigation of the reaction path has revealed the wisdom of including biradical-like structures as shown in Scheme IV. It is acknowledged that **12** and **13** may not represent true intermediates in the sense that they are energy minima, but their position in the proposed mechanism is justified by strong circumstantial evidence. Not only does the inclusion of **12** and **13** readily accommodate the myriad effects of the structural perturbations, but independent generation of electronically excited **12**-like cyclopropyldicarbinyl biradicals does not give the anticipated rearrangement products.[21] Our analysis of the di-π-borate and the cyclopropyl-π-borate rearrangements show, at least in broad outline, a marked parallel to the hydrocarbon cases.

Scheme IV



Direct irradiation of borates **1** and **2** leads to the predominant formal [1,2] shift of a phenyl group to form boratirene **4** and boratirane **5**, respectively. For obvious reasons, we designate this the di-π-borate rearrangement. Attempts to sensitize rearrangement of **1** or **2** with triplet xanthone were unsuccessful. This result finds meaningful parallel in the observation that direct, but not triplet-sensitized, irradiation of *trans*-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene initiates the di-π-methane rearrangement.[22]

Scheme V shows a proposed mechanism for the di-π-borate rearrangement of borate **1**. If the sp^3-hybridized boron atom is viewed as an "insulator", singlet excitation of this substance may be localized on either a phenyl or the phenylethynyl chromophore. Comparison of the absorption spectra of **1** with that of tetraphenylborate indicates that the phenylethynyl group has the lower singlet energy. Excitation at 254 nm will excite both groups. In the proposed mechanism, coupling of a phenyl group to a phenyl group along path b from the upper excited state of borate **1** leads to the minor products of this reaction. The major product arises from reaction along path a, where coupling of phenylethynyl and phenyl groups leads to intermediate boratiranyldicarbinyl biradical anion **14**. The difference in efficiency between the photochemistry of dimethyl-containing borates and the triphenyl-substituted examples may be explained by partitioning of this biradical anion. Cleavage of the bond labeled α in biradical anion **14** moves the reaction along the di-π-methane-like path to biradical anion **15** and ultimately to boratirene **4**, the major product. In this case, the odd electron on the boron atom is stabilized by resonance with two phenyl groups. When these groups are replaced by methyl groups, this extra stabilization is absent and regeneration of **1** by cleavage of the bond labeled β in **14** is more probable.

Our studies indicate that the mechanism for the di-π-borate rearrangement of the styryl-substituted borates to generate boratiranes is subject to the same mechanistic considerations as is outlined previously for the phenylethynyl-substituted cases. One meaningful difference is the decrease in the relative amount of phenyl to phenyl group coupling products from irradiation of **2**.

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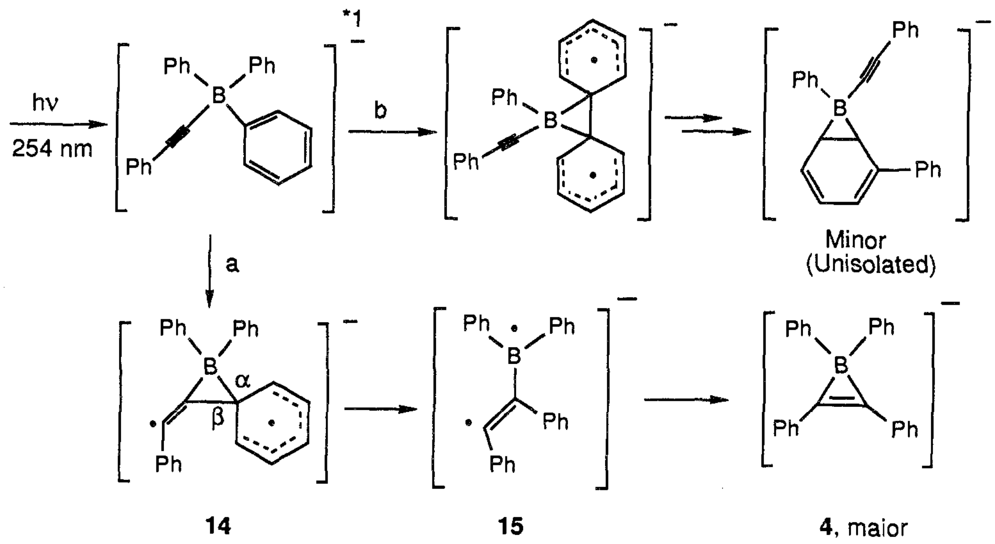
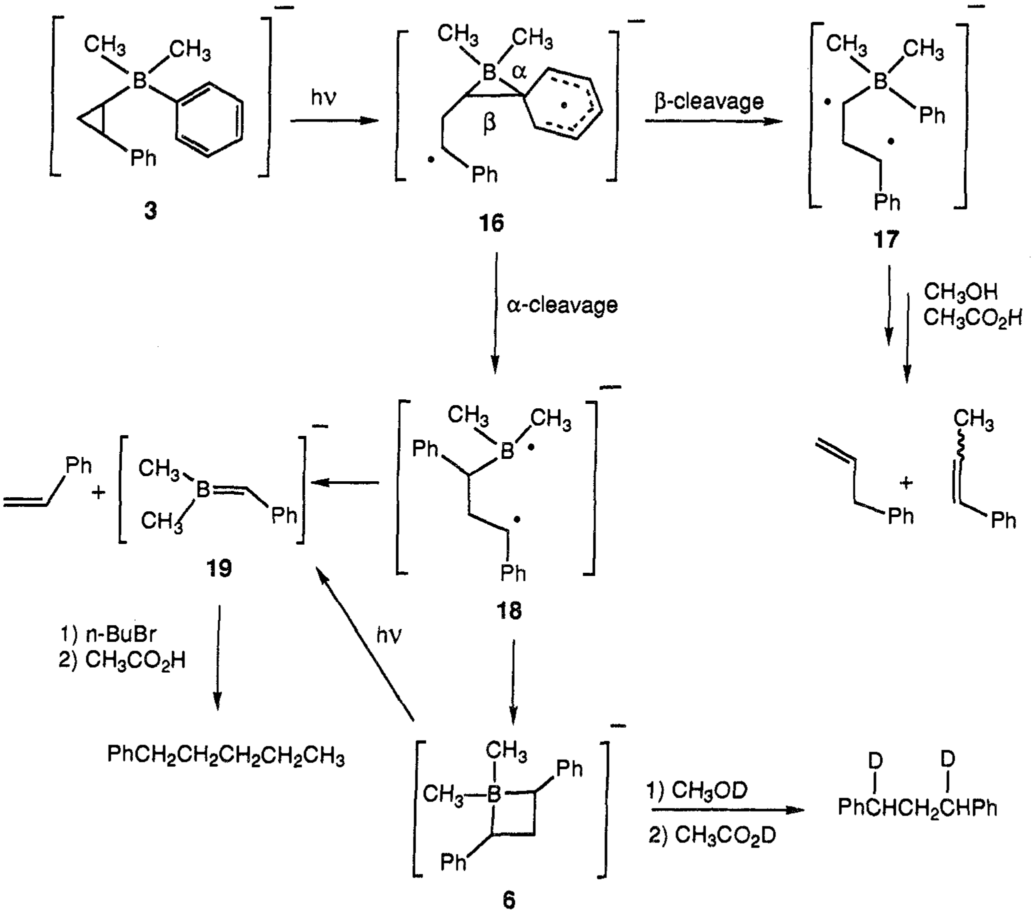
(21) Zimmerman, H. E.; Boettcher, R. J.; Buchler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 7680.

(22) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 1409, 6259, 6267.

Scheme V



Scheme VI



This may reflect a higher extinction coefficient for the styryl group at 254 nm and thus the more likely initial localization of the excitation on this chromophore.

The observed photochemistry of cyclopropyl-substituted borate **3** is apparently closely related to that observed by Zimmerman and co-workers[7] in related hydrocarbon cases. Since we are unable to isolate and characterize suspected boratetane **6**, there is remaining uncertainty about the true reaction course. Nevertheless, analogy to the hydrocarbon examples and the nature of the observed products permit suggestion of the mechanism outlined in Scheme VI.

A significant postulate in the reaction mechanism is the formation of bridged diradical anion **16**. Fragmentation of this intermediate may occur by cleavage of the bond labeled β with formation of **17**, and after workup, this route gives allylbenzene and the β-methylstyrenes. Fragmentation of the bond labeled α in **16** gives biradical anion **18**. Cyclization of **18** leads to boratitane **6**, whose presence is indicated by formation of the dideuteriodiphenylpropane. The formation of amylbenzene when the irradiation of **3** is performed in the presence of *n*-butyl bromide may signal the formation of boron-stabilized carbanion **19**.[23] This anion may arise from fragmentation of **18** or by secondary photolysis of **6**.

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(2) Chemical and Physical Properties of Boratirene 4 and Boratirane 5. The perturbation of electronic and structural properties by the replacement of a carbon by a boron atom is a topic of expanding theoretical and experimental interest.[24] In most of the previously examined cases, electrically neutral trivalent boron atoms are used to simulate isoelectronic and nearly isosteric carbocations. Similarly, the boron atoms of the borates considered in this work can be thought of as negatively charged analogues of neutral carbon atoms. Boratirene **4** and boratirane **5** are the first examples of the three-membered-ring borates to be isolated and characterized.

The chemical properties of **4** and **5** are characteristic primarily of easily oxidized organometallic compounds. Thus, protonation of **4** or **5** gives the demetalated hydrocarbon and for **4** probably (the alternative is less likely double inversion) occurs with retention of configuration at both metalated carbon atoms.

Reduction of **4** with diimide gives **5**. Since *cis*-1,1,2,3-tetraphenylboratirane is the expected primary product of this reaction, we suppose that some path operates to convert the first-formed cis isomer to the isolated trans isomer. The most likely path is ring opening to form an intermediate substituted benzyl anion. This would be followed by bond rotation and recyclization to the isomeric boratirane. The ring-opened anion cannot be detected in the NMR spectrum of **5**, so it must be considerably higher energy than this isomer.

The reactions of **4** and **5** with oxygen might proceed by an electron-transfer path. The reduction potential of oxygen is ca. −0.78 V (vs SCE). The attempts to determine the oxidation potential of **4** and **5** by cyclic voltammetry give irreversible waves. Nonetheless, these measurements indicate that reduction of oxygen to superoxide by the boratirene or the boratirane is thermodynamically possible. Oxidation of the borate converts a two-electron carbon–boron bond to a one-electron bond in the boranyl radical. We have shown in other cases that fragmentation of the one-electron bond to give a borane and a carbon-centered radical is a rapid process.[25] For the present cases, these ring-opened carbon radicals can combine with oxygen (or superoxide) and logically give the observed reaction products.[26]

One of the most intriguing features of boratirene **4** is its color. Similarly substituted cyclopropenes, the all-carbon analogues, absorb only in the deep-UV spectral region and are colorless. We considered that the source of the visible and near-UV absorption bands for **4** might be a small amount of the strongly absorbing ring-opened substituted benzyl anion in equilibrium with the cyclic isomer that is detected by NMR spectroscopy and confirmed by X-ray crystallography. This possibility is eliminated by the low-temperature absorption experiment. The near-UV and visible absorption intensities are still present when the sample is cooled to liquid nitrogen temperature.

The farther-red absorption of boratirene **4** compared to its hydrocarbon analogues may be interpreted similarly to the related phenomenon in the boratanorcaradienes.[2,3] Simply put, the reduction in nuclear charge accompanying conversion of the carbon atom to the anionic borate results in a decrease in the energy separating the HOMO and LUMO orbitals primarily for electrostatic reasons.[27]

Experimental Section

General Procedures. ^{1}H NMR spectra were measured with a Varian XL-200 or a GE QE-300 spectrometer; chemical shifts are referenced to TMS ($CDCl_3$ solvent) or calculated from residual CHD_2CN in CD_3CN solution. ^{11}B NMR spectra were obtained with a GE QE-300NB spectrometer at 96 MHz; chemical shifts are referenced to external $BF_3{\cdot}OEt_2$ (δ 0.00). Mass spectral data were obtained with a Varian CH-5 spectrometer or by GC/MS with a Hewlett-Packard 5970 mass-selective detector (EI, 70 eV) in line with a Hewlett-Packard 5890 GC. Drybox operations were conducted in a N_2 atmosphere purified with a Vacuum Atmospheres Co. Dri-Train MO 40-1 purifier. Melting points are uncorrected. Glassware, where required, was oven dried (150 °C) and cooled in a N_2 atmosphere. Acetonitrile was freshly distilled from calcium hydride under N_2. THF and ether were distilled from sodium/benzophenone, and benzene was distilled from sodium. Other solvents, unless otherwise specified, were commercial samples used without further purification. Microanalyses were performed by the Microanalytical Laboratory, School of Chemical Sciences, University of Illinois.

Potassium Triphenyl(phenylethynyl)borate (1). A 15-mL portion of a 1.6 M *n*-butyllithium solution was added with stirring to a cold (−78 °C) solution of phenylacetylene (2.55 g, 0.025 mol) in 50 mL of THF. After 1 h, a THF solution containing 6.0 g of triphenylborane was added to the cold solution via cannula. The reaction mixture was warmed slowly to room temperature (RT). The cation was exchanged with potassium chloride and the sample recrystallized from acetonitrile/benzene to give a white powder: 5.8 g (60%); ^{1}H NMR (CD_3CN) δ 6.89 (t, 3 H, 8 Hz), 7.03 (t, 6 H, 8 Hz), 7.14 (t, 1 H, 9 Hz), 7.24 (t, 2 H, 9 Hz), 7.34 (d, 2 H, 9 Hz), 7.39 (d, 6 H, 8 Hz); ^{11}B NMR (CD_3CN) δ −12.3; UV λ_{max} = 259 nm ($\log \epsilon = 4.30\ M^{-1}\ cm^{-1}$), 266 (4.30). Anal. Calcd for $C_{26}H_{20}BK$: C, 81.67; H, 5.27; B, 2.83; K, 10.23. Found: C, 81.85; H, 5.23; B, 2.86; K, 10.13.

Tetramethylammonium Triphenyl(*trans*-β-styryl)borate (2). β-Styryllithium (a mixture of isomers from 4.66 g of β-bromostyrene) in THF solution was prepared by the method of Seebach.[28] A THF solution of triphenylborane was added via cannula to the styryllithium solution. The reaction mixture was kept below −50 °C during the addition and then was warmed to RT. The solvent was removed, and the lithium salts were dissolved in water. Aqueous tetramethylammonium chloride was added to the reaction solution, and the white precipitate that formed was recrystallized acetonitrile/methanol to give 4.4 g (42%): ^{1}H NMR (CD_3CN) δ 3.02 (s, 12 H), 6.05 (dq, 1 H, $J_{(d)} = 18$ Hz, $J_{(q)} = 3.0$ Hz), 6.83–7.30 (m, 20 H), 7.58 (d, 1 H, $J = 18$ Hz); ^{13}C NMR (CD_3CN) δ 56.04, 122.97, 125.28, 125.82, 126.68, 129.07, 131.34, 136.08, 143.44, 159.01 (q, $J = 50$ Hz), 164.43 (q, $J = 49$ Hz); ^{11}B NMR (CD_3CN) δ −9.1; UV λ_{max} = 272 nm ($\log \epsilon = 4.35\ M^{-1}\ cm^{-1}$). Anal. Calcd for $C_{30}H_{34}BN$: C, 85.90; H, 8.17; N, 3.33; B, 2.57. Found: C, 86.04; H, 8.09; N, 3.37; B, 2.42.

Tetramethylammonium *cis*- and *trans*-Triphenyl(2-phenylcyclopropyl)borate. A 13-mL portion of *tert*-butyllithium in pentane (1.7 M, 0.022 mol) was added dropwise to a stirred, cold (−100 °C) 2.2-g (0.011-mol) sample of 1-bromo-2-phenylcyclopropane[29] (as a mixture of isomers) in 20 mL of THF. After the addition, the bath temperature was increased to −50 °C and a THF solution of 2.7 g (0.011 mol) of triphenylborane was added dropwise to the reaction mixture. The solvent was removed, and the resulting oil was dissolved in water. The water solution was washed twice with hexane, and an aqueous solution of tetramethylammonium chloride was added. Fractional recrystallization gave pure isomers, both as white crystals the (trans isomer in 3% yield and the cis isomer in 20% yield).

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Trans: ^{1}H NMR (CD_3CN) δ 0.22 (m, 1 H), 0.58 (m, 1 H), 0.82 (m, 1 H), 0.92 (m, 1 H), 3.03 (s, 12 H, $(CH_3)_4N^+$), 6.79–7.17 (m, 20 H); ^{11}B NMR (CD_3CN) δ −9.5. Anal. Calcd for $C_{31}H_{36}BN$: C, 85.90; H, 8.37; N, 3.23; B, 2.49. Found: C, 85.61; H, 8.55; N, 3.33; B, 2.51.

Cis: ^{1}H NMR δ 0.53 (m, 1 H), 0.92 (m, 2 H), 2.06 (m, 1 H), 3.02 (s, 12 H), 6.41 (d, 2 H), 6.57–6.87 (m, 12 H), 7.18 (bs, 6 H); ^{11}B NMR (CD_3CN) δ −10.5. Anal. Calcd for $C_{31}H_{36}BN$: C, 85.90; H, 8.37; N, 3.23; B, 2.49. Found: C, 85.96; H, 8.16; N, 3.21; B, 2.61.

Tetrabutylammonium (*cis*-2-Phenylcyclopropyl)dimethylphenylborate. A solution containing 1.35 g (6.9 mmol) of 2-phenyl-1-bromocyclopropane (as an 8:2 mixture of cis and trans isomers) in THF was cooled to −78 °C. With stirring, an 8.1-mL (1.7 M, 13.8-mmol) portion of *tert*-butyllithium was added slowly to the solution. Meanwhile, a second flask was charged with 1.10 g (6.9 mmol) of dichlorophenylborane and was cooled to −78 °C. A 4.6-mL (3 M, 14.0-mmol) portion of methylmagnesium bromide in ether was added to the frozen dichlorophenylborane. The mixture was placed in an ice bath, and 30 mL of ether was added to the mixture. As the phenyldichloroborane melts, a vigorous reaction occurs forming a white precipitate. The ether solution was added all at once to the (2-phenylcyclopropyl)lithium solution. The combined reaction mixture was warmed to RT, and the solvent was removed. The resulting oil was dissolved in water, and the solution was extracted twice with hexane. Addition of tetrabutylammonium chloride to the aqueous layer gave a white precipitate. Recrystallization from acetonitrile and ether gave 650 mg (16%) of a white solid: ^{1}H NMR (CD_3CN) δ −0.78 (q, 3 H, J = 6 Hz), 0.71 (q, 3 H, J = 6 Hz), 0.07 (m, 1 H), 0.61 (m, 2 H), 0.95 (t, 12 H, 6 Hz), 1.33 (m, 8 H, J = 6 Hz), 1.57 (m, 8 H), 1.85 (m, 1 H), 3.04 (m, 8 H), 6.73 (t, 1 H), 6.89–7.15 (m, 7 H), 7.38 (m, 2 H); ^{11}B (CD_3CN) δ −17.1. Anal. Calcd for $C_{33}H_{56}NB$: C, 82.99; H, 11.82; N, 2.93; B, 2.26. Found: C, 82.95; H, 11.85; N, 2.99; B, 2.27.

Tetrabutylammonium (*trans*-2-Phenylcyclopropyl)dimethylphenylborate. The procedure described for the cis isomer was followed with 1.51 g (7.6 mmol) of 2-phenyl-1-bromocyclopropane (~7:3 mixture of trans to cis isomers). Workup and purification gave 600 mg (13%) of white crystals: ^{1}H NMR (CD_3CN) δ −0.51 (m, 6 H), −0.06 (m, 1 H), 0.43 (m, 1 H), 0.62 (m, 1 H), 0.95 (t, 12 H, J = 6 Hz), 1.33 (m, 9 H, J = 6 Hz), 1.57 (m, 8 H), 3.05 (m, 8 H), 6.70–7.10 (m, 8 H), 7.40 (m, 2 H); ^{11}B NMR (CD_3CN) δ −17.4.

Cesium Phenyl(2-phenylcyclopropyl)dimethylborate (3). The same procedure followed as for the tetrabutylammonium salt gave a mixture of isomers (cis:trans = 2:3). Attempts to purify and separate the isomers by recrystallization were unsuccessful. The borate used in these studies, though a mixture of isomers, was pure as judged by ^{11}B and ^{1}H NMR and elemental analysis: ^{11}B NMR (CH_3CN) δ −17.0, −17.4 (2:3). Anal. Calcd for $C_{17}H_{20}BCs$: C, 55.47; H, 5.48; B, 2.94; Cs, 36.11. Found: C, 55.70; H, 5.54; B, 2.97; Cs, 35.93.

Tetrabutylammonium (Phenylethynyl)dimethylphenylborate. An ether solution of methylmagnesium bromide (8.0 mL, 24 mmol) was added to frozen (−78 °C) dichlorophenylborane (1.91 g, 12 mmol). The reaction mixture was warmed slowly to 0 °C, and then 30 mL of ether was added. The ether solution was removed from the precipitated salts and added to an ether solution of lithium phenylacetylide (1.1 equiv). The solution was warmed to RT with stirring, the solvent was removed, and the resulting oil was dissolved in water and extracted with hexane. Tetrabutylammonium chloride (ca. 3 g) was added to the filtered reaction mixture, and the resulting solid was collected by filtration. Recrystallization form acetonitrile/ether gave white crystals: ^{1}H NMR (CD_3CN) δ 7.20 (m, 10 H), 3.06 (m, 8 H), 1.57 (m, 8 H), 1.35 (m, 8 H), 0.96 (m, 12 H), −0.21 (s, 6 H); ^{11}B NMR (CH_3CN) δ −20.3; ^{13}C NMR δ 133.32, 131.57, 128.92, 126.82, 125.47, 122.66, 59.24, 24.25, 20.29, 13.78. UV (CH_3CN) λ_{max} = 263 nm (ϵ_{max} = 22 000 M^{-1} cm^{-1}). Anal. Calcd: C, 83.27; H, 11.35; N, 3.03; B, 2.34. Found: C, 83.24; H, 11.38; N, 3.03; B, 2.33. The cesium salt was prepared by a similar procedure.

Cesium (*trans*-Styryl)dimethylphenylborate. An ether solution of methylmagnesium bromide (6.0 mL, 18 mmol) was added to frozen (−78 °C) dichlorophenylborane (1.43 g, 9 mmol). The reaction mixture was warmed slowly to 0 °C, and 30 mL of ether was added. The ether solution was removed from the precipitated salts and then added to an ether solution of *trans*-β-styryllithium (1.1 equiv). The solution was warmed to RT with stirring, the solvent was removed, and the resulting oil was dissolved in water and extracted with hexane. Cesium chloride (ca. 2 g) was added to the filtered reaction mixture, and the resulting solid was collected by filtration. Recrystallization from THF/CH_2Cl_2 gave white crystals: ^{1}H NMR (CD_3CN) δ 6.8–7.4 (m, 11 H), 6.2 (d of q, 1 H), −0.21 (q, 6 H); ^{11}B NMR (THF) δ −17.4. UV (CH_3CN) λ_{max} = 272 nm (ϵ_{max} = 19 000 M^{-1} cm^{-1}). Anal. Calcd: C, 54.28: H, 5.13; B, 3.05; Cs, 37.54. Found: C, 54.16; H, 5.10; B, 3.08; Cs, 37.36.

Potassium 1,1,2,3-Tetraphenylboratirene (4). A N_2-saturated THF solution of borate **1** (3.0 g, 7.8 mmol, 100 mL) in a quartz flask was irradiated at 254 nm with stirring. Aliquots were removed during the irradiation and were analyzed by ^{11}B NMR spectroscopy. Resonances characteristic of a boratanorcaradiene structure were observed at δ 1.29 (m), 1.39 (d), 5.65 (dd), 5.86 (d), and 6.04 (dd). When **1** was completely consumed, acid hydrolysis of an aliquot gave a mixture of *cis*-stilbene, biphenyl, and dihydrobiphenyl. The reaction flask was transferred to the drybox, and 200 mL of hexane was added to the mixture. The solid that precipitated was collected by filtration (50% crude yield). Recrystallization from a THF/hexane mixture gave a yellow solid: ^{1}H NMR (THF-d_8) δ 6.79 (t, 2 H), 6.95 (m, 6 H), 7.13 (t, 4 H), 7.52 (t, 8 H); ^{11}B NMR (THF) δ −16.1; ^{13}C NMR (THF) δ 122.00, 123.65, 126.08, 127.70, 128.31, 134.35, 141.79, 149.56 (broad), 161.06 (broad); UV (THF) λ_{max} = 269 nm (ϵ = 21 500), 350 (4500), 450 (600).

Tetramethylammonium *trans*-1,1,2,3-Tetraphenylboratirane (5). An CH_3CN solution of tetramethylammonium styryltriphenylborate (**2**; 0.015 M) in a quartz tube was irradiated under N_2 in a Rayonet reactor equipped with 254-nm lamps. The solvent was removed after the irradiation in a stream of dry N_2. Subsequent operations were carried out in the drybox. The crude solid was recrystallized from acetonitrile/ether and gave a white powder: ^{1}H NMR (CD_3CN) δ 2.40 (bs, 2 H), 3.02 (s, 12 H), 6.57 (m, 2 H), 6.79–6.93 (m, 14 H), 7.24 (m, 4 H); ^{11}B NMR (CD_3CN) δ −9.4; ^{13}C NMR (CD_3CN) δ 38.31 (b), 55.99, 119.99, 123.18, 126.02, 126.62, 127.51, 136.12, 154.85, 158.74 (m); UV λ_{max} = 280 nm (log ϵ = 4.20 M^{-1} cm^{-1}). Anal. Calcd for $C_{30}H_{34}BN$: C, 85.91; H, 8.17; N, 3.33; B, 2.58. Found: C, 85.66; H, 8.10; N, 3.38; B, 2.62.

Potassium *trans*-1,1,2,3-Tetraphenylboratirane: White crystals; ^{1}H NMR (CD_3CN) δ 2.39 (bs, 2 H), 6.57 (m, 2 H), 6.79–6.93 (m, 14 H), 7.24 (d, 4 H); ^{11}B NMR (CD_3CN) δ −9.4.

Tetraphenylarsonium *trans*-1,1,2,3-Tetraphenylboratirane. An acetonitrile solution containing 45 mg (0.12 mmol) of potassium boratirane **4** was combined with an acetonitrile solution containing 50 mg (0.12 mmol) of tetraphenylarsonium chloride. The reaction mixture solution was filtered to remove the precipitated potassium chloride. Removal of the solvent left yellow crystals: ^{11}B NMR (CD_3CN) δ −9.4.

Reduction of Boratirene 4 with H_2 over Lindlar's Catalyst. A THF solution containing 30 mg (0.08 mmol, 10 mL) of potassium boratirene and 50 mg of Lindlar's catalyst was stirred under H_2 (ca. 1 atm) until the yellow color characteristic of the boratirene disappeared. Analysis of the reaction mixture by ^{11}B NMR spectroscopy showed two borohydrides (δ −6.9 (d, J = 80 Hz), −11.7 (d, J = 80 Hz)) in a ratio of 4:1. Addition of trifluoroacetic acid to the reaction mixture decomposed the borohydrides and gave bibenzyl and *cis*-stilbene. The ^{1}H NMR spectrum of the major borohydride product, precipitated from the crude reaction mixture with cyclohexane, shows two peaks consistent with a borohydride: a multiplet at δ 6.05 (vinyl proton) and a quartet at δ 3.25 (J = 80 Hz). Both peaks collapsed to singlets upon decoupling of the boron atom.

Reduction of Boratirene 4 with Diimide. The diimide precursor, anthracene-9,10-diimine, was prepared by the method of Corey and Mock.[13] A N_2-saturated THF solution containing 30 mg (0.072 mmol, 10 mL) of boratirene **4** was heated at reflux, and small portions of the diimide precursor were added until the yellow color of **4** was no longer apparent. The ^{11}B NMR spectrum of the reaction mixture showed that the resonance of boratirene **4** at δ −16 was replaced by a peak at δ −9.6. The product was precipitated by addition of cyclohexane and shown to be boratirane **5** by comparison of its ^{1}H NMR spectrum with an authentic sample.

Reaction of Potassium Boratirene 4 with Dimethyl Sulfate. A N_2-saturated THF solution containing 13.2 mg (0.035 mmol) of **4** and 17.3 mg (0.14 mmol) of dimethylsulfate was stable at room temperature. Heating this solution over a steam bath caused consumption of the boratirene. The reaction was quenched with trifluoroacetic acid and analyzed by GC and GC/MS. The predominant products observed were *cis*- (20%) and *trans*-α-methylstilbene (10%) and 1,1,2-triphenylpropene (5%), identified by comparison of GC/MS data with authentic samples.

Reaction of Potassium Boratirene 4 with Methyl Iodide. An N_2-saturated acetonitrile solution containing 9.9 mg (0.026 mmol) of **4** and 5.3 mg (0.037 mmol) of methyl iodide reacted when heated over a steam bath. The reaction mixture was quenched with trifluoroacetic acid. Analysis of the solution by GC and GC/MS showed *cis*-stilbene (40%) and *cis*- and *trans*-α-methylstilbene (12% and 6%, respectively). The products were identified by comparison of GC/MS data with authentic samples.

Reaction of 5 with Oxygen. A solution of 15.5 mg (0.026 mmol) of **5** and 4 mg of hexamethylbenzene (internal standard) in 3 mL of CD_3CN was purged with oxygen for 30 min. ^{11}B NMR spectroscopy showed that boratirane **5** had been completely consumed. The reaction mixture was heated at reflux for 45 min and then analyzed by ^{1}H NMR spectroscopy. Stilbene oxide (45%, δ 3.95) and boratolanes **9** (20%; δ 4.40 (s, (+/−)), 5.18 (s, meso)) were observed. Addition of trifluoroacetic acid to the reaction mixture followed by gentle reflux caused the absorptions at δ

4.40 and 5.18 to be replaced by signals at δ 5.99 and 5.36. The new signals were assigned to the ring proton of the *meso*- and (+/–)-borolanes by comparison with authentic samples.

(+/–)-**2,4,5-Triphenyl-1,3,2-borolane:** ^{1}H NMR (CD_3CN) δ 5.36 (s, 2 H), 7.36–7.92 (m, 15 H); ^{11}B NMR (CD_3CN) δ 28; MS (GC/MS, EI) *m/e* 300 (M^+, base), 222, 193, 90.

***meso*-2,4,5-Triphenyl-1,3,2-borolane:** ^{1}H NMR (CD_3CN) δ 5.99 (s, 2 H), 7.01–7.98 (m, 15 H); ^{11}B NMR (CD_3CN) δ 32; MS (GC/MS, EI) *m/e* 300 (M^+, base), 222, 193, 90.

Photolysis of Tetramethylammonium (2-Phenylcyclopropyl)triphenylborate in the Presence of CH_3OH. The borate (64.2 mg, 0.15 mmol) in a N_2-purged solution (10 mL of acetonitrile and 1.0 mL of CH_3OH) was irradiated at 300 nm in a Rayonet reactor. Analysis of the solution by GC after the borate has been consumed shows the formation of biphenyl, dihydrobiphenyl, and 1,3-diphenylpropane in a ratio of ca. 1:1:1.

Photolysis of Cesium (2-Phenylcyclopropyl)dimethylphenylborate in the Presence of MeOH. A N_2-purged solution of borate **3** (30.6 mg, 0.08 mmol) and 50 μL of methanol was prepared in 3 mL of THF. The irradiation at 254 nm was monitored by ^{11}B NMR spectroscopy and by gas chromatography. The yield of 1,3-diphenylpropane from this reaction was 25%. The other products formed in this reaction were identified by comparison with authentic samples: toluene (2%); styrene (1%); allylbenzene (8%); *cis*-β-methylstyrene (6%); and *trans*-β-methylstyrene (30%).

This reaction was repeated with MeOD (dried over molecular sieves). After the borate was consumed, the solution was quenched with CH_3CO_2D. Analysis by GC/MS showed the presence of dideutierated 1,3-diphenylpropane (80% D_2, see the following text). Collection of this product by preparative GC gave pure 1,3-diphenylpropane-*1,3-d*$_2$: MS (EI, GC/MS) *m/e* 198 (M^+), 106, 93 (base); ^{1}H NMR ($CDCl_3$) δ 1.95 (m, 2 H), 2.63 (t, 2 H), 7.18–7.31 (m, 10 H). For deuterium-incorporation analysis, the region around the parent ions was scanned and averaged over entire peak: natural abundance *m/e* 196 (100), 197 (17), 198 (1); deuteriated *m/e* 198 (100), 197 (27), 196 (2).

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Cyclobutene Photochemistry.[1] Reinvestigation of the Photochemistry of *cis*- and *trans*-Tricyclo[6.4.0.0^{2,7}]dodec-1-ene

William J. Leigh*,[2a] and Kangcheng Zheng[2b]

Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1.

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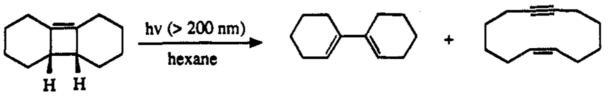
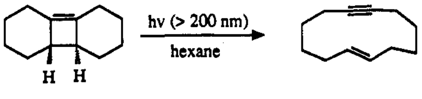
Abstract: The direct photolyses of *cis*- and *trans*-tricyclo[6.4.0.0^{2,7}]dodec-1-ene in hydrocarbon solution have been reinvestigated with 193-nm, 214-nm, and broad-band UV (>200 nm) light sources. The two compounds undergo competitive stereospecific fragmentation (yielding *cis*- or *trans*-cyclododec-7-en-1-yne, respectively) and ring opening (yielding 1,1′-bicyclohexenyl). The observation of 1,1′-bicyclohexenyl formation from *both* cyclobutene isomers differs from the results of a previous study of the photochemistry of these compounds, which concluded that only the cis isomer undergoes ring opening upon photolysis in solution, presumably via a disrotatory electrocyclic pathway. The present results verify the conclusions of several recent studies that the photochemical ring opening of alkylcyclobutenes in general proceeds nonstereospecifically.

Introduction

Several years ago, it was reported that direct photolysis of *cis*-tricyclo[6.4.0.0^{2,7}]dodec-1-ene (*cis*-**1**) in hydrocarbon solution affords 1,1′-bicyclohexenyl (**2**) and *cis*-cyclododec-7-enyne (*cis*-**3**) as the major products (see eq 1).[3] Photolysis of the trans isomer (*trans*-**1**) under similar conditions, on the other hand, was reported to afford only *trans*-cyclododec-7-enyne (*trans*-**3**; see eq 2). For many years, the results of this study have provided the prototypical examples illustrating the stereochemistry associated with two fundamental photochemical pericyclic reactions:[4] the electrocyclic ring opening of cyclobutene and the ($\sigma_{2s} + \sigma_{2s}$) cycloreversion reaction of four-membered cyclic hydrocarbons. Until recently,[5-9] this study has provided the only example that illustrates the stereochemistry of the former reaction.



cis-**1** **2** *cis*-**3** (1)



trans-**1** *trans*-**3** (2)

Simple orbital symmetry selection rules,[4] as well as more sophisticated ab initio theoretical calculations,[10] predict that the

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(1) Part 5 of the series. Part 4: see ref 8.

(2) (a) Natural Sciences and Engineering Research Council of Canada University Research Fellow, 1983–1993. To whom correspondence should be addressed. (b) Permanent address: Department of Chemistry, Zhongshan University, Guangzhou, People's Republic of China.

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